# Electronic Supplementary Information (ESI)

## Mechanism of structural changes and crystallization kinetics of amorphous red phosphorus to black phosphorus under high pressure

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# Experimental Procedures

**Chemicals.** Amorphous red phosphorus (>99.99%) was purchased from Sigma-Aldrich and used without further purification.

**Preparation for High-Pressure Experiments.** High-pressure experiments were carried out using diamond anvil cell with diamonds having 400-μm cults. A 200-μm thick T301 stainless steel gasket was indented to 45 μm, where a 130 μm hole was made by spark eroding using electrical discharge machining. Powder samples were load into the pin hole in a glove-box filled with nitrogen and sealed by DAC. The pressures were measured by the ruby fluorescence technique.

**Raman Spectroscopy.** The Raman system adopted a backscattering geometry, and the scattered light was dispersed using an imaging spectrograph equipped with a 1200 lines/mm grating, achieving a resolution of 0.20 $cm^{-1}$. The Raman signal was then recorded using an ultrasensitive liquid-nitrogen-cooled, back-illuminated CCD detector from Acton. The 780 nm diode pumped solid state laser was used as an exciting source. The laser beam was focused onto a spot with the diameter of approximately 5 μm using an objective microscope. The Raman band of the silicon wafer at 520.7 $cm^{-1}$ was used to calibrate the spectrometer. Data acquisition was two times 10-s accumulations at the pressure below 3.00 GPa and one time 120 s accumulations.

**High-resolution transmission electron microscopy (HRTEM).** The structure of as-made transition products by high pressure was characterized by transmission electron microscope (FEI Tecnai G2 F20 S-TIWN) operated at 200 kV. The reclaimed samples were retrieved from the DAC in a nitrogen filled glove box. Then they were dispersed in anhydrous ethanol and drop cast onto TEM grids. After being dried by an infrared heater, it was transferred into the sample chamber as quickly as possible to minimize possible degradations in black phosphorus like structure caused by exposure in air.[1-4]

## Results and Discussion

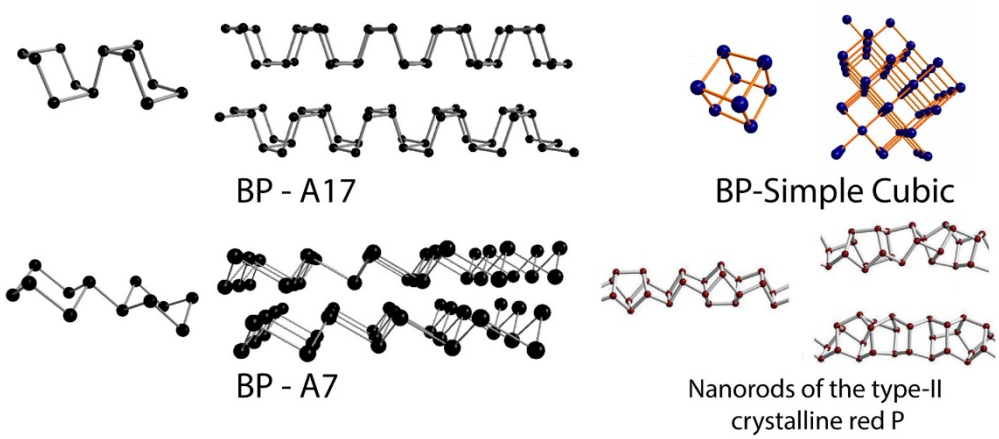


**Figure S1** Structure models of black phosphorus in A17, A7 and simple cubic phases, and phosphorus nanorods of type II crystalline red phosphorus.

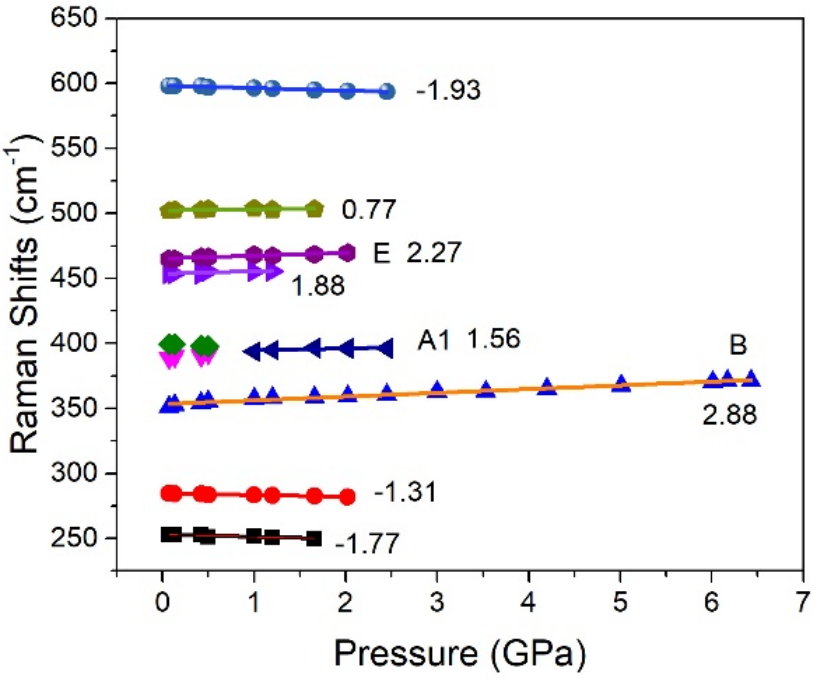


**Figure S2** The pressure dependency of peak shifts of ARP in the region of 200-600 $cm^{-1}$. Pressure dependence of Raman shifts derived from linear fitting for each mode is listed in the graph.

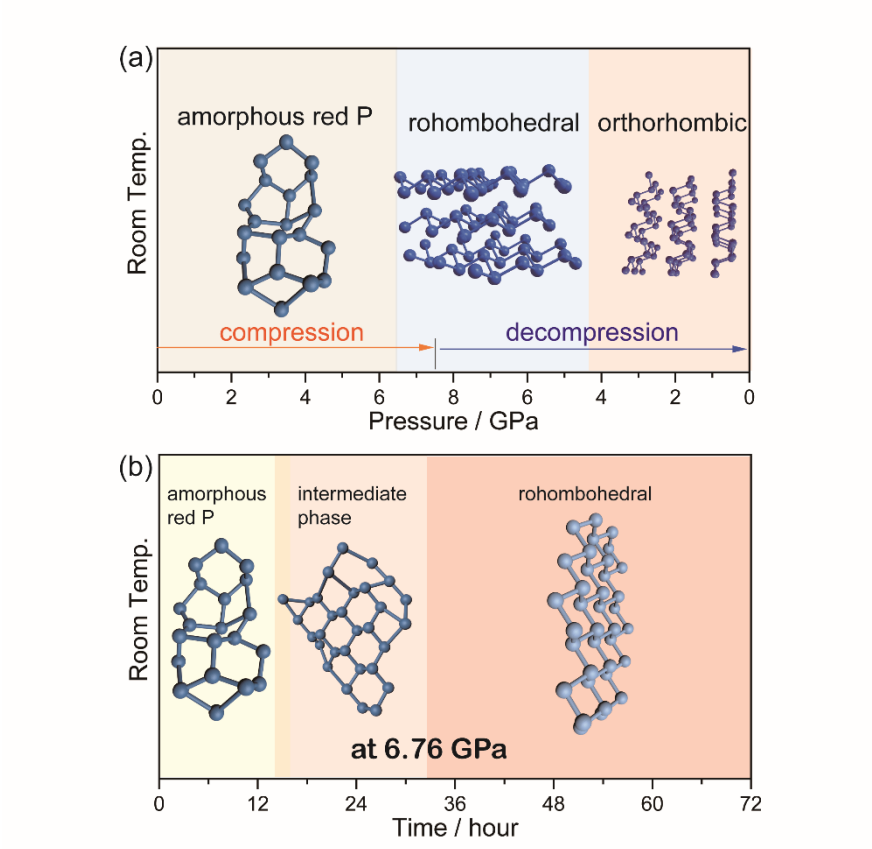


**Figure S3** Schematic phase diagrams showing structural transitions under compression and decompression with amorphous red phosphorus as starting material (a) and time-dependent structural evolution of amorphous red phosphorus at fixed pressure of 6.76 GPa(b).

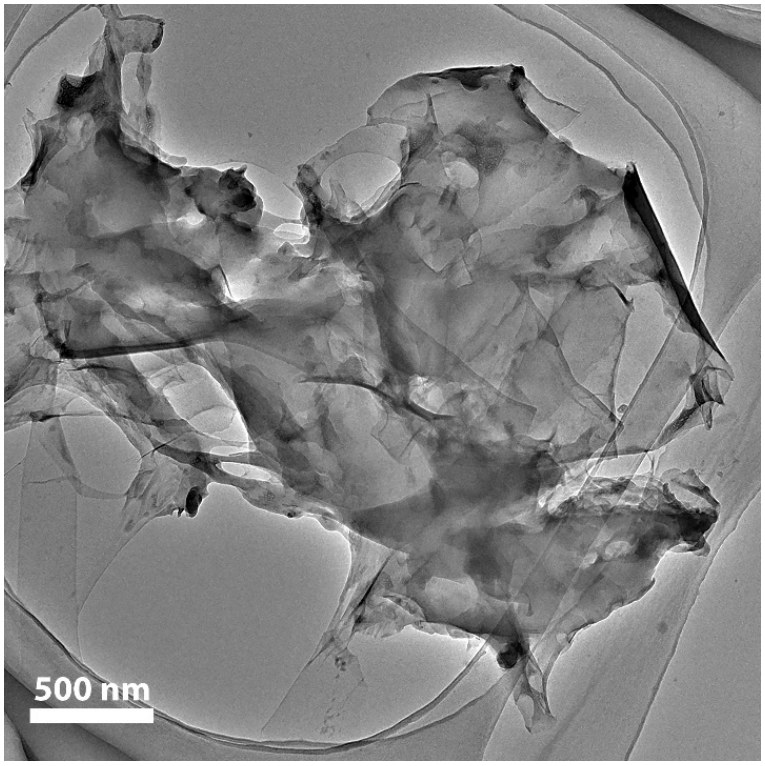


**Figure S4** TEM image of reclaimed sample at fixed pressure of 6.76 GPa after dwelling for 36 hours.

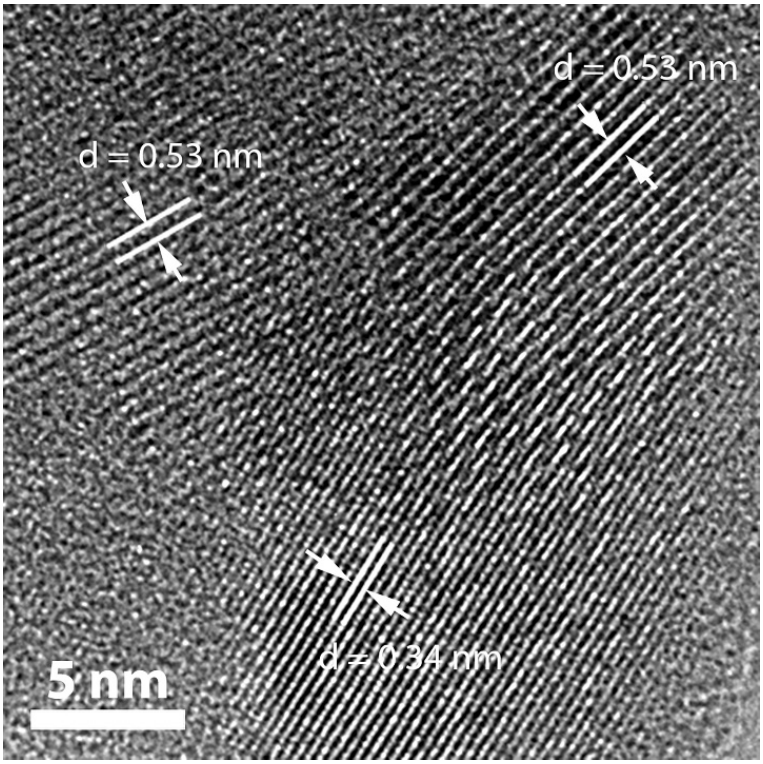


**Figure S5** TEM image showing twinning crystal formed under high pressure.

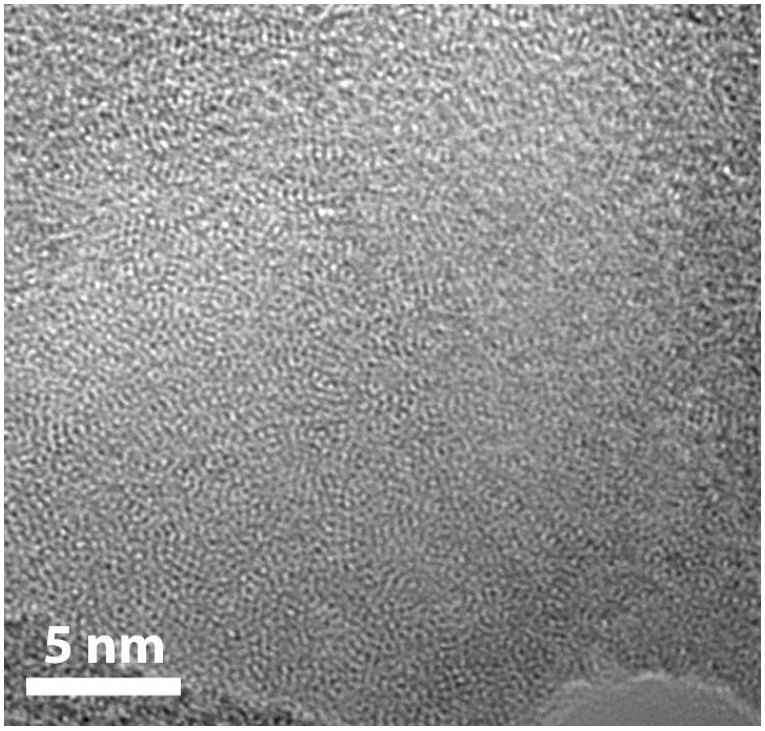


**Figure S6** HRTEM image of amorphous region (I) in Fig 3a of reclaimed ARP.

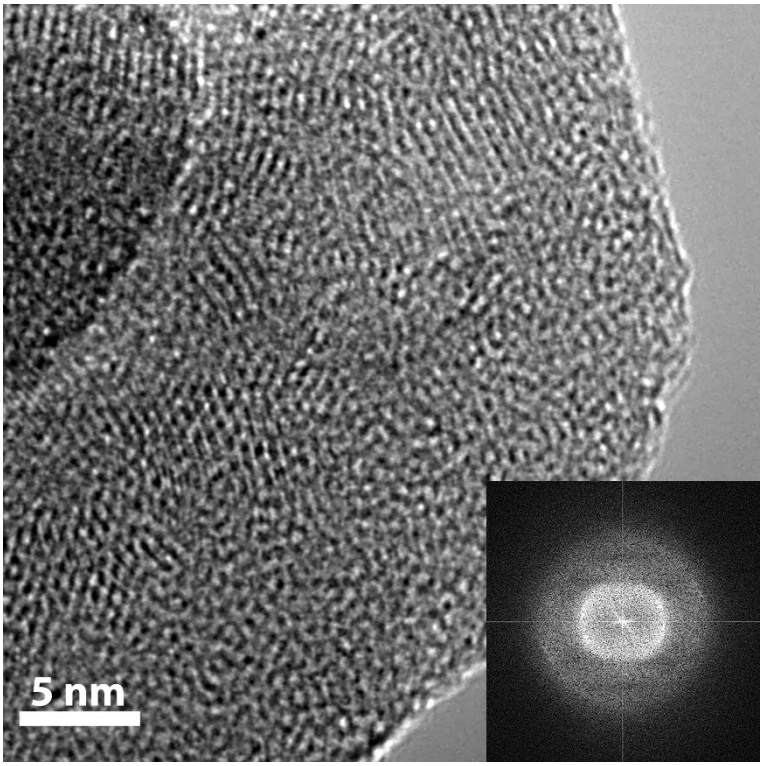


**Figure S7** HRTEM image of structure of intermediate phase (region III of Fig. 3a). The inset shows FFT pattern suggesting the amorphous nature.

**References**


1. H. Liu, Y. Du, Y. Deng and P. D. Ye, *Chemical Society Reviews*, 2015, **44**, 2732-2743.
2. A. Favron, E. Gaufrès, F. Fossard, A.-L. Phaneuf-L'Heureux, N. Y. W. Tang, P. L. Lévesque, A. Loiseau, R. Leonelli, S. Francoeur and R. Martel, *Nature Materials*, 2015, **14**, 826.
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